Nitrogen substitution of carbon in graphite: Structure evolution toward molecular forms

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A series of randomly nitrogen-substituted carbon clusters in graphitelike structures, containing up to 96 carbon atoms, is theoretically investigated through semiemipirical pseudopotential techniques. The evolution of conformation and electronic structure is obtained as a function of nitrogen content. Results from semiempirical geometry optimizations reveal that the clusters are planar for nitrogen concentrations up to [N]/[C]~20%. Above this concentration, buckling develops in the clusters. One of the characteristics of these corrugated clusters is the presence of carbon dangling bonds. Chemical stabilization imposes that these structures evolve to either a three-dimensional, fully covalent carbon nitride network, or to molecular forms. Among the well-defined molecular structures that could develop in amorphous carbon nitride, we found nanotubules and a molecular cage of elemental compositions CN and C_3N_4, respectively. [S0163-1829(98)06943-4]

INTRODUCTION

The present availability of reliable theoretical modeling methods combined with increasingly powerful computational resources has allowed the development of molecular and crystal modeling as an area in materials science. The computational design of materials for specific applications has a striking example, the search for super-hard materials. Recent interest in carbon nitride materials originated from the theoretical prediction of C_3N_4 solids that would present mechanical and optical properties comparable to those of diamond.[1] Despite recent advances to produce this material, reasonable amounts of crystalline carbon nitride for proper characterization has not yet been obtained.[2–4] From the chemical point of view, it is known that the C_3N_4 phase should be very difficult to synthesize due to the well-known trend of carbon and nitrogen to form multiply bonded compounds. Indeed, in most experiments the material produced is amorphous and may have microcrystallites of carbon nitride with the desired composition, but the total incorporation of nitrogen is usually below the ideal 3:4 composition.[5,6]

In this work we theoretically investigate the evolution of conformation and electronic structure of a large graphitic carbon cluster randomly substituted by nitrogen, as a function of nitrogen content. Cluster calculations are convenient to investigate the bonding capabilities of amorphous systems like most carbon nitride materials reported in the literature. The development of three-dimensional covalently bonded CN_x structures are predicted to occur for [N]/[C] concentrations greater than 20%. Distortions from the graphitic structure are pronounced at high nitrogen content, which might lead to the growing of closed molecular forms. Indeed, we found examples of such molecules: a molecular cage and nanotube forms with C_3N_4 and CN stoichiometries, respectively. This paper is organized as follows: In the next section we present the theory employed in this study, followed by a detailed discussion of the results. The last section is devoted to the conclusions.

THEORY

The conformation of graphitic clusters including up to 96 carbon atoms was obtained through the Parametric Model 3 (PM3) semiempirical method.[7] Bonds at the boundaries were saturated with hydrogen. Nitrogen substitution was simulated through random replacement of carbon atoms such that N-N bonds were avoided. Systems presenting the concentrations [N]/[C]=0.07, 0.14, 0.17, 0.20, 0.23, 0.37, and 1.00 were studied. Two sets of optimizations were carried out: one set imposing C_s symmetry to maintain the planar arrangement of the atoms, and the other set allowing full optimization of atomic coordinates. These calculations were performed within the packages SPARTAN (Ref. 8) and GAMESS.[9]

The electronic structure of the optimized molecules was obtained through the use of the valence effective Hamiltonian (VEH) method. This is an *ab initio* pseudopotential technique derived from Hartree-Fock theory which has been successfully applied to carbon materials.[10,11] Histograms representing the density of states (DOS) were obtained through the usual counting of one-electron states. A small contraction factor of VEH-energy spectrum (0.94 in the present case, the same adopted in Ref. 11) must be applied in order to correct the well-known tendency of Hartree-Fock theory in producing bands that are wider than those experimentally observed. Histograms were convoluted using Gaussian line shapes with a broadening of 0.5 eV. The above procedure has already been applied to amorphous carbon nitride materials. It proved to be a reliable tool to assist in the interpretation of ultraviolet photoemission spectra (UPS).[11]

The DOS profiles were used for the interpretation of the structure evolution upon N doping of graphite and those associated with closed molecular forms. Therefore, a common zero of energies was adopted for all systems. It was chosen to be the Fermi energy of the pure graphite cluster. Also, the densities were normalized for comparison purposes, since the clusters may have a different number of atoms.

RESULTS AND DISCUSSION

The geometrical optimization of an hexagonal graphitelike cluster containing 96 carbon and 24 hydrogen atoms, and subsequent evaluation of the electronic structure resulted in the DOS displayed in Fig. 1. The dotted line corresponds to the density associated with the empty (conduction band) states. Also shown in this figure is the UPS spectrum of amorphous graphite taken from Ref. 11. The basic features

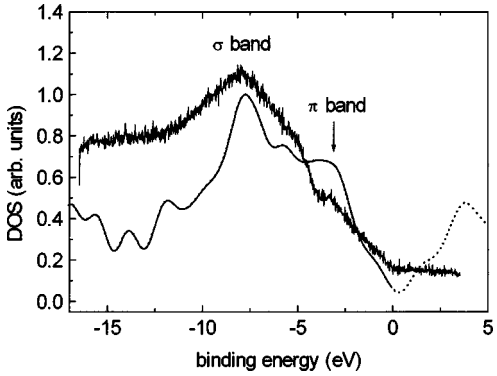


FIG. 1. Density of states (arb. units) of a 96 carbon atom hexagonal cluster calculated by the VEH technique. The Fermi energy has been shifted to 0. Occupied and empty states are represented by the continuous and dotted lines, respectively. The ultraviolet photoemission spectrum of amorphous graphite is shown for comparison (Ref. 11).

of the top of the valence band are quite well reproduced by the VEH spectrum, with a structure at ~3.5 eV binding energy associated with electrons coming from π bonds and a wide band peaking at ~7.9 eV binding energy, which is associated with electrons involved in C $2p$-σ bonds. Relative intensities are not expected to be well reproduced since we have not used photoemission cross sections in the theoretical DOS evaluation. This cluster has a gap of 1.8 eV, corresponding to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

The optimized graphite cluster was then used to generate a series of randomly N-substituted clusters such that N-N bonds were avoided. These calculations are aimed at investigating the stability of the planar graphene sheets upon N substitution. Thus, in a first set of geometry optimizations the C_s symmetry was imposed so as to keep the clusters in a plane. The corresponding stimulated DOS are shown in Fig. 2 for some selected [N]/[C] concentrations. The dotted lines represent the DOS associated with empty states, as in Fig. 1. As the N content increases, σ and π bands continuously shift towards larger binding energies and electrons fill antibonding π^* states, above the graphite Fermi energy. As expected, the

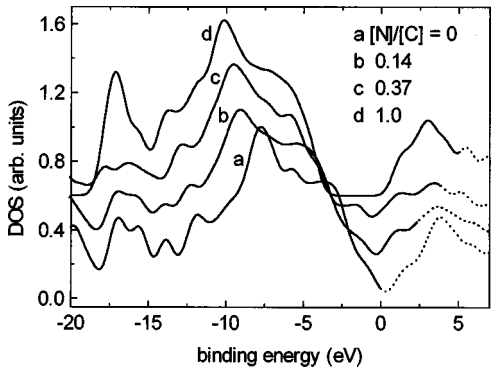


FIG. 2. Evolution of the DOS for planar clusters of N-substituted graphite upon increasing the N content. [N]/[C] from a to d: 0%, 14%, 37%, and 100%. Dotted lines represent the density associated with empty (π^*) states. Bands associated with σ and π electrons are systematically shifted to larger binding energies on increasing the N content, and the occupation of π^* states increases.

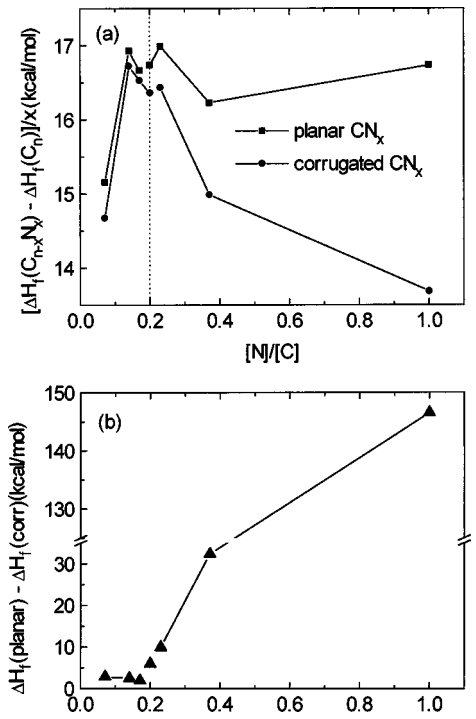


FIG. 3. Differences of heats of formation (ΔH_f) as a function of the [N]/[C] concentration. In (a), the average enthalpy associated with N incorporation into graphite is plotted for planar (squares) and corrugated (circles) clusters, whereas in (b) the difference in total enthalpies between planar and corrugated clusters is shown. The lines are only guides to the eye.

HOMO–LUMO gaps decrease, from 1.8 eV in the pure carbon cluster to 0.18 eV in the saturated, [N]/[C]=1.0 cluster, due to the filling of conduction-band states. This result confirms our earlier report on the evolution of the DOS upon N substitution of graphite, but now with clusters twice as large.[11]

In the second set of geometrical optimizations the atomic coordinates were allowed to fully relax. An important result obtained here is that, for nitrogen concentrations below 20%, the optimized structure maintain the planar geometry. Beyond that, distortions around the nitrogen atoms appear and become more important as more nitrogen atoms are incorporated. Heats of formation (ΔH_f) obtained from PM3 calculations are shown in Fig. 3 as a function of the [N]/[C] concentration. Results from a single cluster representative of a given nitrogen concentration were used in this figure. Various distributions of substitution sites were tested and the average difference in total enthalpies was ~1–2 kcal/mol per nitrogen atom. We evaluated the quantity $[\Delta H_f(C_{n-x}N_x) - \Delta H_f(C_n)]/x$, where n is the total number of heavy atoms. This is the average energy associated with nitrogen incorporation [Fig. 3(a)]. Two sets of points are shown, corresponding to planar and corrugated clusters. We notice that the behavior below 20% is quite similar for both types of clusters. Corrugated clusters have slightly smaller energies mainly due to nitrogen atoms that are placed at the cluster boundaries, where larger relaxation is expected. Above 20% this figure shows a clear preference for the clusters to lose the graphitic geometry. This result also suggests that there is an energy barrier against nitrogen incorporation into graphite. Once the system is allowed to relax to a more three-

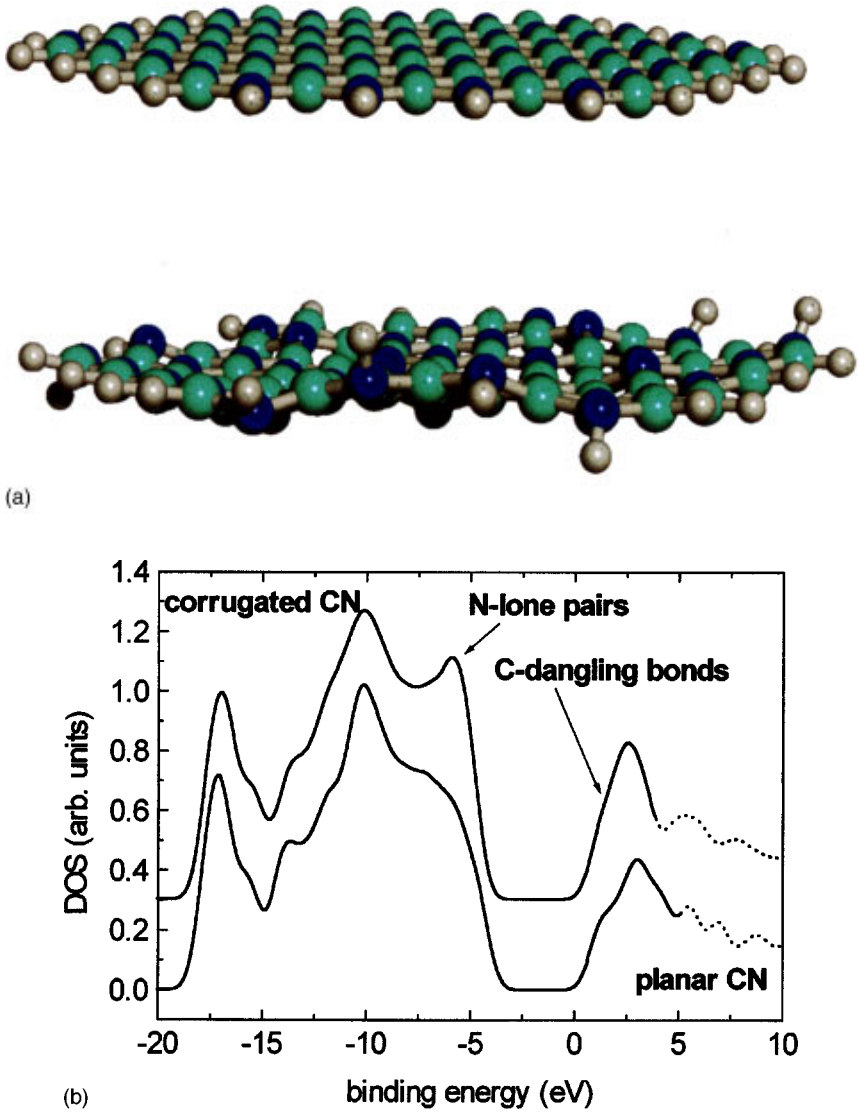
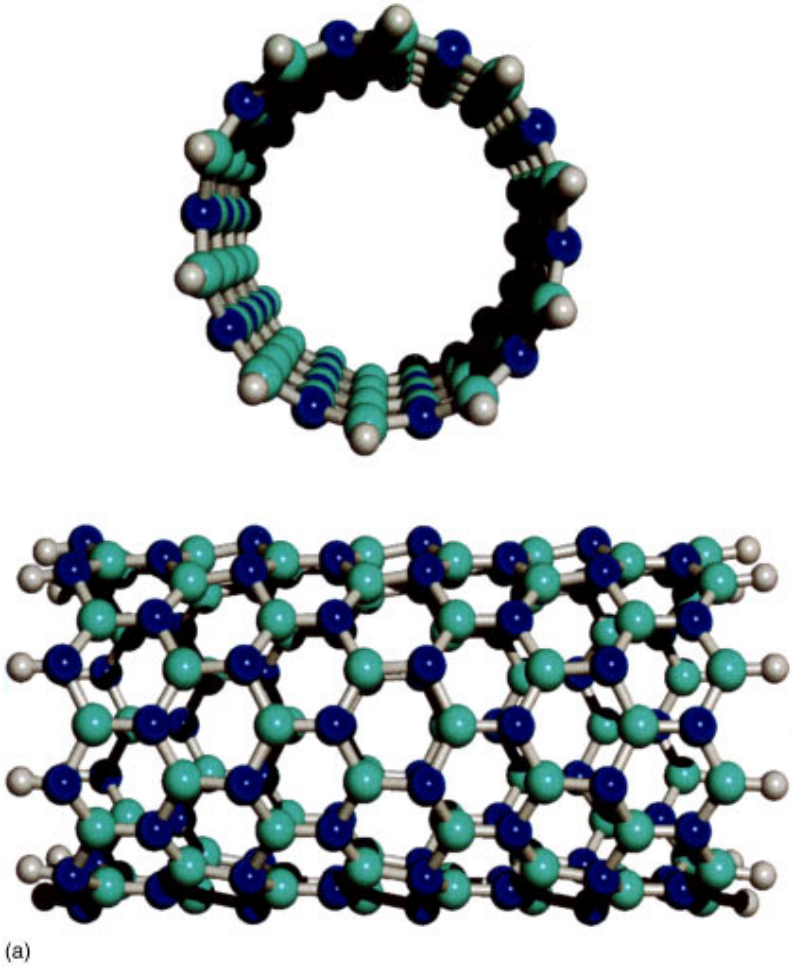


FIG. 4. (a) (Color) Ball-and-stick models for the optimized geometries of planar (top) and corrugated (bottom) CN clusters. Atom labeling: C (cyan); N (blue); H (gray); (b) DOS (arb. units) corresponding to the structures shown in (a). The dotted lines are the densities associated to empty states.

dimensional structure, this barrier decreases so that the energy cost for incorporating more nitrogen atoms is smaller at high [N]/[C] content. This is consistent with the experimental reports about the difficulty in obtaining high nitrogen contents in carbon nitride samples prepared from graphite targets. Figure 3(b) depicts the difference in total heat of formation between planar and corrugated clusters. Here, the abrupt transition of the heats of formation at the concentration 20% is more clearly seen. We point out that, in our earlier experimental report[11] on the evolution of UPS spectra of amorphous CN_x, a significant modification of the top of the valence band was observed for nitrogen concentrations larger than 20%. The growth of a nitrogen lone-pair band at 5.0-eV binding energy for [N]/[C]>20% was evidenced in the spectra. This was interpreted as an indication of the three-dimensional character of the amorphous material.

Figure 4(a) shows a ball-and-stick model of the optimized planar and corrugated CN clusters. The transition from graphitic to corrugated conformation could be interpreted by noting that the total number of states is preserved upon N replacement of C in graphite, since the total number of atoms is fixed. Hence, the excess of electrons coming from the nitrogens occupy the antibonding π^* levels, which tend to destabilize the planar geometry. In our calculations, the filling of 10% (i.e., half the nitrogen concentration) of antibonding levels gives the system enough electronic energy to overcome the barrier that separates planar and corrugated structures. The system then distorts to lower the electronic energy and electrons localize in nitrogen lone pairs. This interpretation is further supported by the molecular-orbital analysis of the electronic states near the Fermi energy. The DOS of planar and corrugated systems at [N]/[C]=1.0 are shown in Fig. 4(b). From the molecular-orbital analysis we identified the band at 5.0-eV binding energy in the corrugated CN cluster as coming from N lone pairs. The Fermi energy shifts to lower energies when compared to the planar CN cluster. Moreover, the structure which was formerly associated to antibonding π^* levels becomes a structure of carbon dangling bonds. This means that the corrugated clusters are not chemically stable and subsequent evolution of the structure is expected. Cross-linking between neighboring sheets could be anticipated, due to the dangling bonds and to



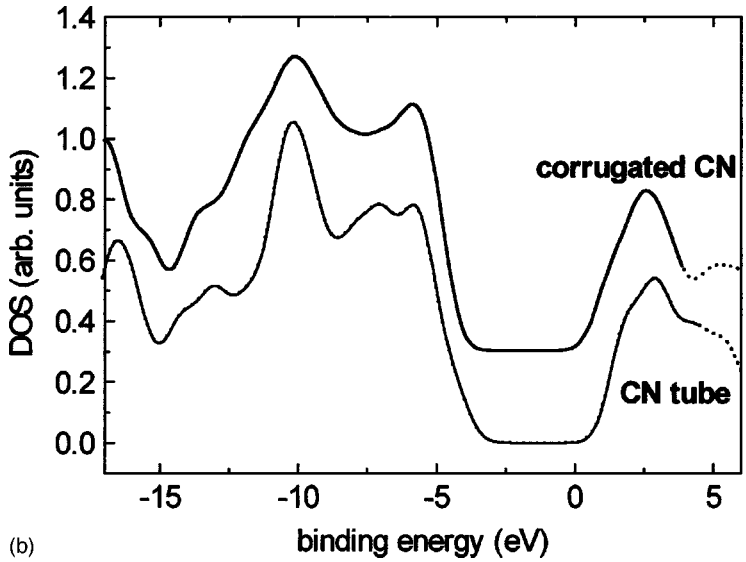


FIG. 5. (a) (Color) Ball-and-stick models of the top and lateral views of the molecular CN tube. Atom labeling: C (cyan); N (blue); H (gray); (b) DOS (arb. units) of the molecular CN tube shown in (a) and the corrugated CN cluster.

the increased volume of the buckled structures. For instance, in the corrugated cluster shown in Fig. 4(a), some of the nitrogen atoms relax to positions that are ~0.7 Å above and below the basic plane.

Among the several possibilities of new systems that could grow from N-doped graphite due to the buckling of the structure, we investigated some molecular forms. A natural consequence of the curvature induced by nitrogen doping is the rolling of the cluster to form a tubule. Carbon nitride tubules have already been proposed in the literature,[12,13] as well as tubules from the $C_xN_yB_z$ family of compounds.[14] There are several ways of rolling a sheet of two-dimensional CN sys-

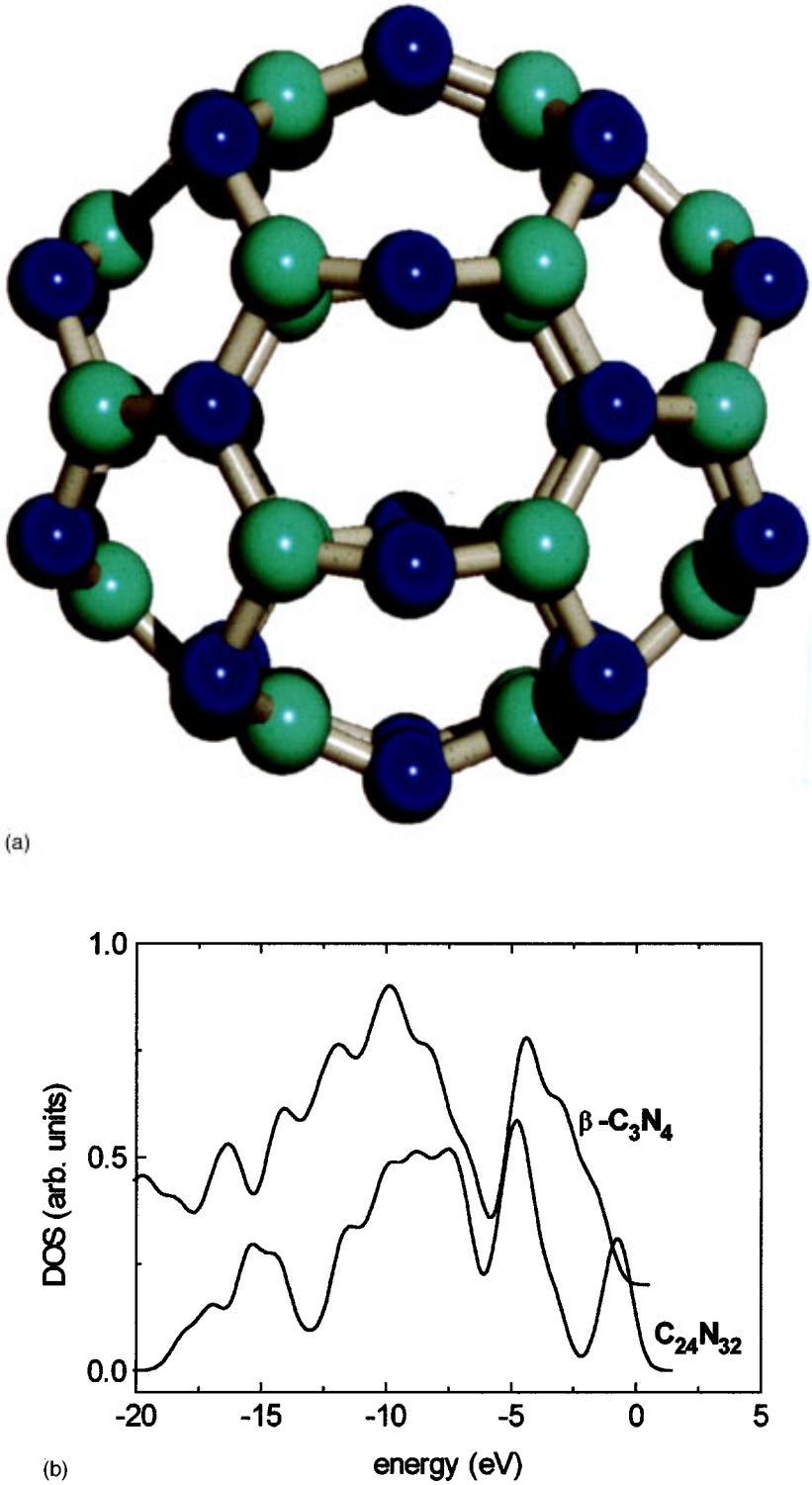


FIG. 6. (a) (Color) Ball-and-stick model of the molecular cages $C_{24}N_{32}$—atom labeling: C (cyan); N (blue); (b) DOS (arb. units) of the molecular cage shown in (a) and a cluster of 36 C and 48 N atoms obtained from the predicted β-C_3N_4 crystal structure (from Ref. 11).

tem to form a tubule. Interestingly, the different closures of the sheets give rise to cylindrical molecules having diverse electric dipole moments, varying from zero to a maximum value. We found the most stable tubule structure to be the one in which there are C-N bonds pointing along the tube axis direction, as shown in Fig. 5(a). This is also the molecule with highest dipole moment.

Geometry optimizations based on the PM3 technique were performed on several tubule molecules, always saturating the end bonds with hydrogen. The largest tube we obtained within our computational resources is shown in Fig. 5(a), which contains 180 atoms. An important difference between our fully optimized tubule structure and the one reported in Ref. 12 is the modulation of C-N bonds along the tube axis (in Ref. 12 the partial geometry optimization did not result in any modulation). An alternating pattern of longer (1.46 Å) and shorter (1.35 Å) C-N bonds resulted, and it is coupled to a modulation of the tube diameter, from 7.76

to 8.34 Å. This seems to be related to the Peierls instability[15] which is usually observed in quasi-one-dimensional systems. This means that half of the nitrogen atoms contribute two electrons to the π system while the other half of the N atoms have a localized lone pair, so that this tube has the same number of π electrons as that of a pure carbon tubule. A rough estimate of the strain energy associated with the tube closure from the buckled CN structure gave 110 kcal/mol or 4.8 eV per molecule. This results in ~0.06 eV per CN for a tube having ten CN pairs along the circular base of the tube.

A comparison between the DOS profiles of a corrugated CN cluster and the CN tube is illustrative of the chemical stabilization provided by the tube formation [Fig. 5(b)]. Together with the lone-pair peak at ~0.5 eV binding energy and the structure associated with CN-σ bonds at ~10.0 eV, another structure appears at ~7.0 eV due to the formation of π bonds. Also the feature corresponding to carbon dangling bonds is absent from the tubule DOS.

These molecular tubes are expected to growth in an amorphous CN_x material, even below the ideal 1:1 stoichiometry. As commented in the Introduction, many experimental methods employed to prepare carbon nitride materials produce samples where nitrogen is not uniformly incorporated. Hence, other molecular forms of CN_x could be present in real samples provided that one allows for the variation of the relative [N]/[C] concentration. CN analogs of fullerene cages are not possible because of the five-membered rings. However, we found that increasing the relative N concentration, a high symmetry molecular cage with the composition $C_{24}N_{32}$ was obtained, which belongs to the C_3N_4 family of compounds. The molecular structure is shown in Fig. 6(a). This molecule has C_{4h} symmetry and its building blocks are eight-membered connected rings resembling the structure of β-C_3N_4. Notice that the nitrogens are not all equivalent: eight of them have connectivity 3 and the remaining 24 nitrogens have connectivity 2. The bonds around a connectivity of 3 nitrogen are 1.47 and 1.48 Å in length and are not all in the same plane. Bond angles vary from 117° to 119°. Connectivity two atoms, on the other hand, show typical aromatic bonds of 1.36 Å and bond angle of 120°. All carbons are in equivalent sites, with all the bonds in the same plane.

The stability of this cage could be estimated through the enthalpy of the reaction:

$$\tfrac{2}{3}C_{48}N_{48}H_{24} \rightarrow C_{24}N_{32} + \tfrac{1}{12}C_{96}H_{24} + 7H_2$$

for which the enthalpies of formation of all compounds have already been determined. This results in $\Delta H = 533.4$ kcal/mol $= 0.41$ eV/atom. For comparison purposes, a PM3 geometrical optimization of the buckyball C_{60} has been performed and the enthalpy of the reaction

$$\tfrac{5}{8}C_{96}H_{24} \rightarrow C_{60} + \tfrac{15}{2}H_2$$

resulted in $\Delta H = 495.5$ kcal/mol $= 0.36$ eV/atom, which is close to the value found in the literature for the relative binding energy of C_{60} compared to a graphene sheet.[16] These results suggest that the molecular cage $C_{24}N_{32}$ could be found in carbon nitride materials having high nitrogen content.

In Fig. 6(b) we plotted the DOS of the molecular cage and the one obtained from a cluster representative of β-C_3N_4, taken from Ref. 11. The β-C_3N_4 cluster contains 36 C and 48 N atoms, and the electronic structure was obtained using the same methodology as used here. The lone-pair structure is shifted into two peaks in the molecular cage, due to the distinct nitrogen sites. Since this molecule has as network of π bonds, the peak at 10.0-eV binding energy, clearly seen in β-C_3N_4 DOS, is less pronounced in the spectrum of the molecular cage. It merges into the π density, which peaks at ~7.5 eV.

One interesting aspect of finding closed molecular forms of carbon nitride in the stoichiometry 3:4 is the availability of synthetic routes to produce these cages, which could be used as a starting material to a solid-state synthesis of β-C_3N_4. Similar attempts have already been reported in the literature, as the precursor synthesis of C_3N_4 films through high-pressure treatment of $C_3N_3F_2R_2$ molecular crystals (R is a suitable radical).[17] More recently, the successful synthesis of C_3N_4 from the precursor azaadenine, $C_4N_6H_4$, has been reported.[18] Organic synthesis has also been shown to produce bowl-shaped polycyclic aromatic molecules that are organic analogs of half the C_{60} buckyball—the so-called buckybowls.[19]

CONCLUSIONS

In this paper we presented a conformation/electronic structure study of N-substituted graphitelike clusters by means of semiempirical PM3 and pseudopotential VEH theoretical methods. We found a transition from planar to corrugated structures upon N incorporation for concentrations above 20%. Buckling of the structure leads to localization of electrons into lone-pair orbitals. This is in agreement with the experimental observation[11] of lone-pair bands in the photoemission spectrum of amorphous carbon nitride for nitrogen concentrations above 20%. Buckling and 180° bending of the graphitic planes of $CN_{0.2}$, from high-resolution transmission electron microscopy of sputtered thin films, have also been reported in the literature.[20] For compositions approaching the 1:1 stoichiometry the corrugated clusters are not chemically stable due to the emergence of carbon dangling-bond states near the Fermi energy. This implies that it is possible to grow three-dimensional CN materials or closed molecular forms, such as nanotubules and molecular cages. We have been able to theoretically characterize a family of nanotubes with open ends, having dipole moments ranging from zero to a maximum value, depending on how the CN sheets are rolled to form the tube. The highest dipole moment tube is also the most stable molecule. Another possibility for a closed molecular structure is the $C_{24}N_{32}$ molecular cage, a system belonging to the C_3N_4 family of compounds.

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